

Charge Modulations vs. Strain Waves in Resonant X-Ray Scattering

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A method is described for using resonant x-ray scattering to separately quantify the charge (valence) modulation and the strain wave associated with a charge density wave. The essence of the method is a separation of the atomic form factor into a “raw” amplitude, $f_R(\omega)$, and a valence-dependent amplitude, $f_D(\omega)$, which in many cases may be determined independently from absorption measurements. The advantage of this separation is that the strain wave follows the average quantity $|f_R(\omega) + \langle v \rangle f_D(\omega)|^2$ whereas the charge modulation follows only $|f_D(\omega)|^2$. This allows the two distinct modulations to be quantified separately. A scheme for characterizing a given CDW as Peierls-like or Wigner-like follows naturally. The method is illustrated for an idealized model of a one-dimensional chain.

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Charge density waves (CDWs) are pervasive in condensed matter, arising in di- and trichalcogenides, conducting polymers, transition metal oxides etc. However they may form by a variety of mechanisms. The best understood is the Peierls mechanism in which a gap at the Fermi level opens, and a charge (valence) modulation forms, through the presence of a strain wave. The basis for the Peierls mechanism is the electron-phonon interaction which drives pairing between an electron and a hole with equal but opposite wave vector, \mathbf{k}_F , resulting in a charge modulation with total momentum $2\mathbf{k}_F$. A CDW may also be driven by electron interactions, however, an idealized example being the Wigner crystal (WC) ground state of a dilute electron gas, which is driven by direct Coulomb[1]. Because of the close analogy between charge density waves and superconductivity [2], and the occurrence of both in many systems such as the dichalcogenides and the copper-oxides in which superconductivity is not clearly understood, it would be extremely useful to distinguish between Peierls-like and Wigner-like (i.e. interaction-driven) mechanisms in practice[3].

The main distinction between a Peierls CDW and a WC is the presence of a lattice distortion in the former case that is not required in the latter. However in any real material even a WC must have at least some incidental lattice distortion if only because of electrostatics. Therefore, in practice, distinguishing between these two phenomena is a quantitative rather than a qualitative matter.

X-ray diffraction is sensitive to both charge modulations and strain waves. Scattering from both can be enhanced, through different resonant mechanisms, by tuning the x-ray photon energy to an atomic core transition, i.e. so-called resonant x-ray scattering (RXS). Here a general method is proposed for using RXS to distinguish between scattering from a charge modulation and scattering from a strain wave, even when the two coexist. This method allows the charge and strain amplitudes to be quantified independently. A system classifying a given charge density wave as either Peierls or Wigner in origin naturally arises from this separation. The method is

demonstrated for the idealized case of a one-dimensional chain.

I. SEPARATING THE ATOMIC FORM FACTOR

In quantum electrodynamics, the cross section for elastic scattering of photons from a material is[4]

$$M_{\mathbf{q}} = \frac{e^2}{2mc^2} \rho_{\mathbf{q}} + \frac{e^2}{\hbar m^2 c^2} \sum_n \frac{\langle 0 | \hat{\mathbf{p}} \cdot \mathbf{A} | n \rangle \langle n | \hat{\mathbf{p}} \cdot \mathbf{A} | 0 \rangle}{\omega - \omega_n + i\gamma} \quad (1)$$

where $\rho_{\mathbf{q}}$ is a Fourier component of the total electron density, \mathbf{q} is the momentum transfer, $\hat{\mathbf{p}}$ is the momentum operator, $\hat{\mathbf{A}}$ is the photon field operator (vector potential), and ω is the photon energy. The first of these two terms is equivalent to classical Thomson scattering, does not depend on ω , and gives rise to the “normal” dispersion of optical constants in matter, i.e. in SI units $\chi_{\mathbf{q}} = -r_e \lambda^2 \rho_{\mathbf{q}} / 4\pi^2$, where r_e is the classical electron radius and $\lambda = 2\pi c / \omega$ [5]. The second, resonant term corresponds to scattering via virtual transitions between core and valence states, is highly dependent on ω , and is the origin of anomalous dispersion[6]. This term, sometimes referred to as the Kramers-Heisenberg formula, has been shown to provide direct sensitivity to valence band charge and spin ordering in condensed matter [7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17], provided ω coincides with an edge threshold.

How can one distinguish between a charge modulation and a strain wave? One might be tempted to just compare the relative sizes of nonresonant and resonant scattering on the assumption that a lattice distortion, which translates all the electrons in an atom including those in the core, contributes mainly to the former and valence band effects mainly to the latter. Indeed, the Kramers-Heisenberg formula alone is normally used to analyze near-edge scattering data [10, 11, 13, 14]. However one must realize two things. First, the valence modulation itself should scatter in the Thomson channel as well since

it corresponds to a real, albeit small, charge modulation. Second, it was realized long ago[18] that the resonant term also contributes to scattering far from the edges via virtual, off-shell processes. The optical constants of Cu metal, for example, exhibit no region of ‘normal’ dispersion from the infrared up to 100 keV[18]. So the resonant term is omnipresent, a trait that is commonly exploited in crystallographic phasing methods[19]. More to the point, both the valence and lattice modulations of a CDW scatter in both channels, and a more appropriate division of the cross section than Eq. 1 is needed.

Here it is proposed to divide the cross section instead into a ‘raw’ and ‘valence-dependent’ component. More specifically, assuming the form factor for an atom, f , is a function of both ω and the valence state, v , it is proposed to make the separation

$$f(\omega, v) = f_R(\omega) + v f_D(\omega). \quad (2)$$

Here f_R is the ‘raw’ part of the atomic scattering factor and f_D describes how it changes with valence[20]. Like the full f , f_R is dimensionless (i.e. ‘electrons’) and converges to Z^* as $\omega \rightarrow \infty$ [5]. f_R contains both resonant and nonresonant processes but only those, such as edge jumps, that are independent of the detailed electronic structure of the atom.

f_D has units of electrons/valence and can be thought of the scattering power of the valence modulation. Like f_R this quantity contains both resonant and nonresonant processes, however the nonresonant contribution will be extremely small. One can expect f_D to be large only for ω near the threshold of an absorption edge, where the intermediate states involve transitions directly into the valence band.

There are two advantages to the division in Eq. 2. First, as will be illustrated in the next section, scattering from a strain wave will follow only $|f(\omega, \langle v \rangle)|^2$, where $\langle v \rangle$ is the *average* atomic valence of the material, while scattering from the valence modulation follows $|f_D(\omega)|^2$. By measuring the photon energy dependence of a CDW reflection, provided f_D and f_R are known, one can determine separately the charge and strain amplitudes as well as their relative phase.

Second, and most importantly, in many cases f_R and f_D can be independently determined from doping-dependent x-ray absorption (XAS) data. More specifically, f is related to the absorption coefficient [5] by

$$\text{Im}[n(\omega, \langle v \rangle)] = -\frac{r_e N \lambda^2}{2\pi V_c} \text{Im}[f_R(\omega) + \langle v \rangle f_D(\omega)] \quad (3)$$

where n is the complex index of refraction, N is the number of atoms in a unit cell, and V_c is the unit cell volume. So, by measuring the absorption coefficient on two or more samples of different $\langle v \rangle$, $\text{Im}[f_R(\omega)]$ and $\text{Im}[f_D(\omega)]$ can be determined by solving a system of equations at each value of ω . The real parts can then

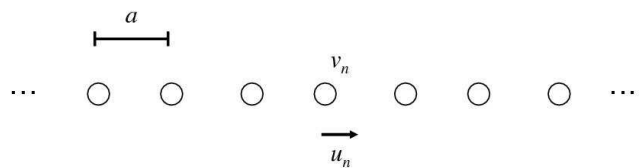


FIG. 1: One-dimensional, monatomic chain. u_n and v_n describe respectively the displacement from equilibrium and valence state of the n th atom in the lattice.

by determined by Kramers-Kronig transform. Without having to appeal to a specific model, then, the charge and strain amplitudes can be determined. XAS acts as a reference against which resonant scattering measurements can be calibrated.

Use of this procedure rests on several assumptions. First, one must assume that the scattering processes are local and that an atomic form factor, f , is definable. This will be valid as long as $v_g \tau \ll \lambda/2$, where v_g is the group velocity of the core electron-hole pair, τ is its radiative lifetime, and λ is the x-ray wavelength. For measurements near edges with sharp white lines, such as the L edges of the transition metals, one can expect this condition to be well satisfied. Next one must assume that changes in XAS spectra due to changes in $\langle v \rangle$, determined by comparing samples with different chemical composition, indeed arise from valence effects and not extrinsic phenomena such as changing crystal structures etc. Next, one must assume that changes in f are small i.e. are linear in v , which should be true as long as the CDW amplitude is not too large. It is *not* necessary that the sample have a rigid or noninteracting band structure. In determining f_R and f_D from XAS one implicitly makes the assumption that the electronic structure of every point in the CDW corresponds to the *average* electronic structure in a sample with that valence. Finally, one assumes that x-ray absorption measurements are a good measure of the forward scattering amplitude, i.e. that there are not hidden loss processes such as photoelectron production. Violation of this last point has already been observed [17] but is not a significant effect.

II. ONE-DIMENSIONAL CHAIN

To see how f_R and f_D enter a resonant scattering experiment consider the idealized case of a one-dimensional, monatomic chain, as shown in Fig. 1. Imposed upon this chain are a longitudinal strain wave, described by a set of displacements u_n , and a valence modulation, described by a set of valence states, v_n . For simplicity it is assumed that the modulations are sinusoidal, i.e.

$$u_n = u_0 \cos(kna) \quad (4)$$

$$v_n = \langle v \rangle + v_0 \cos(kna + \phi) \quad (5)$$

where u_n implies that the n th atom resides at position $r_n = na + u_n$, where a is the average lattice parameter. u_0 and v_0 are the amplitudes of the strain and charge waves, respectively, $\langle v \rangle$ is the average atomic valence, and k is the wave vector of the CDW. The quantity ϕ allows for the fact that, while the two modulations have the same wave vector, there may be a phase difference between them.

The integrated intensity of a Bragg reflection is proportional to the square of the scattering amplitude, ρ_q , which is given by

$$\rho_q(\omega) = \frac{1}{N} \sum_{n=1}^N f(\omega, v_n) e^{iqu_n} \quad (6)$$

where $f(\omega, v_n)$ is as defined by eq. (2) and $N = 2\pi/ka$ is the number of sites in the supercell, i.e. the dimensionless CDW period [21]. q is the momentum transfer along the chain and is restricted to discrete values $q = 2\pi l/Na$, where l is an integer. If one multiplies out the terms one arrives at four distinct contributions to the scattering amplitude.

$$\rho_q(\omega) = \rho_q^B(\omega) + \rho_q^v(\omega) + \rho_q^u(\omega) + \rho_q^{uv}(\omega) \quad (7)$$

The first term,

$$\rho_q^B(\omega) = \frac{1}{N} f(\omega, \langle v \rangle) \sum_{n=1}^N e^{iqna}, \quad (8)$$

is the ‘‘Bragg’’ term and corresponds to resonant x-ray scattering off the average lattice. This quantity is independent of u_0 and v_0 and is nonzero whenever $q = 2\pi m/a$, where m is an integer, i.e. at the Bragg points of the undistorted chain. This term always has exactly the value $f(\omega, \langle v \rangle)$, which demonstrates that regular Bragg scattering has the energy dependence of $|f(\omega, \langle v \rangle)|^2 = |f_R(\omega) + \langle v \rangle f_D(\omega)|^2$, i.e. simply tracks the average scattering factor of the atomic lattice. ρ_k^B is highly resonant but nonzero for all values of ω .

The next term

$$\rho_q^v(\omega) = \frac{1}{N} v_0 f_D(\omega) \sum_{n=1}^N \cos(kna + \phi) e^{iqna} \quad (9)$$

is the ‘‘valence’’ term and corresponds to resonant x-ray scattering off the valence modulation. This quantity is nonzero only for $q = \pm k$ and has the value $\rho_k^v(\omega) = v_0 f_D(\omega) \exp(i\phi)/2$. This demonstrates that resonant scattering from the valence modulation tracks only $|f_D(\omega)|^2$ and is proportional to v_0^2 . Since f_D is significant

only near an edge, one can expect to see scattering from a valence modulation only over a narrow energy range near threshold. This is the experimental signature of a valence modulation in resonant x-ray scattering.

The third term is the ‘‘strain’’ term and corresponds to scattering off the lattice distortion. Provided the size of the distortion is small, i.e. $\exp(iqr_n) = \exp(iqna)(1 + iqu_n)$, the strain term has the value

$$\rho_q^u(\omega) = \frac{1}{N} i q u_0 f(\omega, \langle v \rangle) \sum_{n=1}^N \cos(kna) e^{iqna}. \quad (10)$$

This quantity is also nonzero only if $q = \pm k$ and reduces to $\rho_k^u(\omega) = iqu_0 f(\omega, \langle v \rangle)/2$. Scattering from the strain wave is proportional to $(ku_0)^2$, as expected, and like the Bragg term follows $|f(\omega, \langle v \rangle)|^2$ so is visible at all values of ω . Evidently all structural scattering is alike in its adherence to the average $f(\omega, \langle v \rangle)$. Unlike the Bragg term, however, the strain term occurs at the same q as the valence scattering and the two may coherently interfere. We will see that, if this interference is visible, it provides a means to determine the phase shift, ϕ .

The final term is somewhat unexpected and apparently has not been addressed before. It is a mixed term corresponding to coherent displacement of the valence modulation. Written out, it has the form

$$\rho_q^{uv}(\omega) = \frac{1}{2N} i q v_0 u_0 f_D(\omega) \sum_{n=1}^N [\cos(2kna + \phi) + \cos(\phi)] e^{iqr_n} \quad (11)$$

This quantity is nonzero only if $q = \pm 2k$ and, while it arises from both strain and valence scattering, it tracks only f_D . ρ^{uv} is not a multiple-scattering effect; it is a sign that if both charge and strain modulations are present the total modulation is anharmonic. Observation of this term, i.e. by tuning the x-ray energy near threshold and scanning around $2k$, would be a strong validation of our approach. However this term is extremely small.

III. A GENERIC EDGE

The various scattering processes are best illustrated with a specific model of f_R and f_D near an absorption edge for a single atom. As was argued earlier, f_R describes processes that are material- and valence- independent, such as the edge jump, and f_D describes only those processes that depend on the atomic valence, v . As an illustrative model of f_R , we consider a generic edge jump, i.e. a dielectric susceptibility whose imaginary part has the form

$$\text{Im}[\chi(\omega)] = \frac{J}{\omega} \theta(\omega - \omega_e). \quad (12)$$

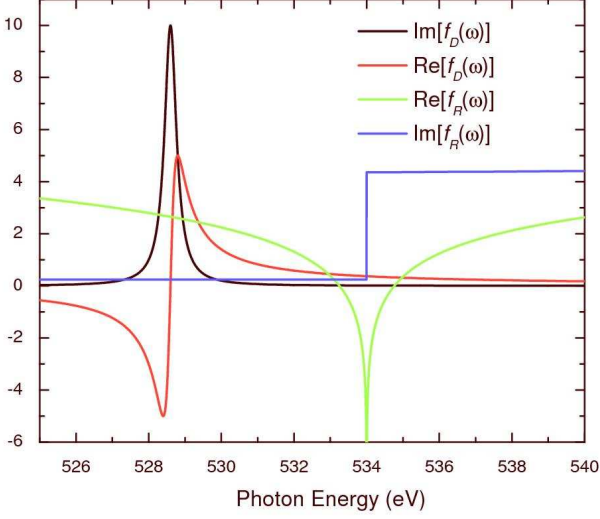


FIG. 2: Real and imaginary parts f_D and f_R as determined from the parameter values chosen (see text).

where ω_e is the edge energy and J is the size of the jump. χ must satisfy the Kramers-Kronig relations so its real part is given by the integral

$$\text{Re}[\chi(\omega)] = \frac{2J}{\pi} \int_{\omega_e}^{\infty} \frac{d\omega'}{(\omega')^2 - \omega^2} = -\frac{J}{\pi\omega} \log \left| \frac{\omega_e - \omega}{\omega_e + \omega} \right|. \quad (13)$$

This can be considered a generic analytic model for an idealized edge. The atomic scattering factor is related to this susceptibility by[22]

$$f_R(\omega) = -\frac{V_c \omega^2}{r_e c^2} \chi(\omega) \quad (14)$$

where χ is in cgs units. V_c here is the volume per atom. Bear in mind that f in general is a tensor, but for simplicity we will treat it as a scalar here. It is important to point out that this quantity actually diverges as $\omega \rightarrow \infty$ but near the edge it is well behaved.

Eq. 14 is for an isolated edge. However in practice there are other transitions that are far away but still contribute to f . To account for these we add a constant “background” scattering factor, f_0 , i.e.

$$f_R(\omega) \rightarrow f_R(\omega) + f_0 \quad (15)$$

Using the notation $f(\omega) = f^1(\omega) + if^2(\omega)$, writing it out explicitly, f_R has the form

$$f_R^1(\omega) = -\Delta \frac{\omega}{\pi\omega_e} \log \left| \frac{\omega_e - \omega}{\omega_e + \omega} \right| + f_0^1 \quad (16)$$

$$f_R^2(\omega) = \Delta \frac{\omega}{\omega_e} \theta(\omega - \omega_e) + f_0^2 \quad (17)$$

where $\Delta = V_c J / r_e c^2$.

The valence-dependent form factor, f_D , could take on many forms. In high temperature superconductors, for example, it actually exhibits a sign change[17]. For present, illustrative purposes, we will simply take it to be a Lorentzian, i.e.

$$f_D(\omega) = \frac{A}{\omega - \omega_0 - i\gamma} \quad (18)$$

In principle f_D should have an energy-independent component representing Thomson scattering from the valence modulation, but in situations of interest this is small.

For numerics, we will take the parameter values $f_1^0 = 9.50$, $f_2^0 = 0.246$, $\Delta = 4.114$, $A = 2$ eV, and $\gamma = 0.2$ eV, $\omega_e = 534$ eV, and $\omega_0 = 528.6$ eV. While it is intended that this illustration be general these parameters are quite a good model of the oxygen K edge. f_R and f_D for these parameter values are plotted in Fig. 2.

For the CDW itself we use the parameters $v_0 = 0.1$ electron, $u_0 = 0.1a$, $k = 2\pi/4a$, and $\langle v \rangle = 0.12$. The scattered intensity at $q = k$ is given by square of the total scattering amplitude, $|\rho_k^u(\omega) + \rho_k^v(\omega)|^2$. The strain and charge scattering amplitudes can coherently interfere, so must be added before squaring. The resulting quantity depends explicitly on the phase, ϕ .

The quantity $|\rho_k^u(\omega) + \rho_k^v(\omega)|^2$ is plotted against energy in Fig. 3. For this plot ϕ is taken to be zero. Spectra are shown for a pure charge wave, a pure strain wave, and a composite wave. Notice that scattering from the charge-only wave is nonzero only in the region in which f_D , displayed in Fig. 2, is nonzero. The strain-only wave, in contrast, is visible at (almost) all energies. This affirms ones intuition that scattering from structural distortions should be visible at all energies, but the valence modulation only near the edge. If both modulations are present the lineshape is not simply the sum of the two because of the non-trivial dependence on the phase factor, ϕ .

To illustrate this phase dependence the line shape is plotted in Fig. 4 for various values of ϕ . Notice that not only the intensity of the various features but in fact the entire spectral lineshape depends sensitively on ϕ . Therefore, if both strain and charge scattering are simultaneously visible, and f_R and f_D are determined independently from XAS, it should be possible to objectively determine the phase from a one-parameter fit to this shape.

IV. PEIERLS VS. WIGNER CDWS

Distinguishing between a Peierls CDW and a more exotic CDW driven by many-body interactions, such as a stripe phase or a Wigner crystal, is a quantitative rather than a qualitative matter. This is because in any real material even a CDW driven purely by electron-electron interactions, because of electrostatics, must still be accompanied by a lattice distortion, though it may be

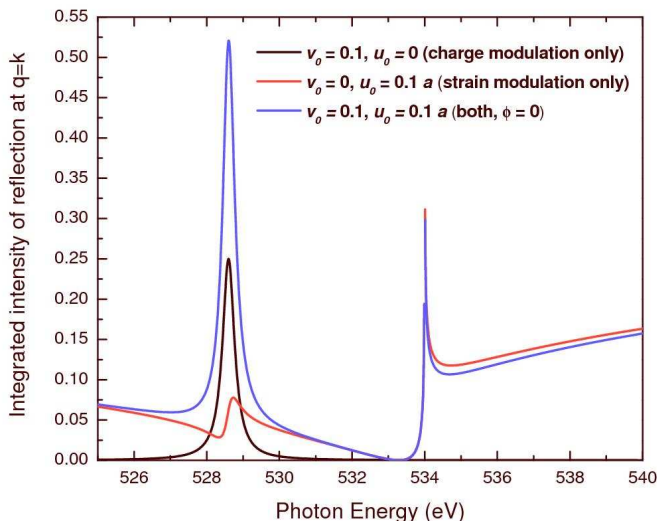


FIG. 3: Plots of the integrated intensity of resonant x-ray scattering at $q = k$, i.e. $|\rho_k^u(\omega) + \rho_k^v(\omega)|^2$. Here $\phi = 0$. (black line) Charge modulation only. (red line) Strain wave only. (blue line) Both charge and lattice modulations present. Charge scattering is localized near threshold but the strain wave, while resonant, is visible at all energies. Notice that the lattice distortion has a strong intensity max at the edge jump due to the cusp in the real part of f_R .

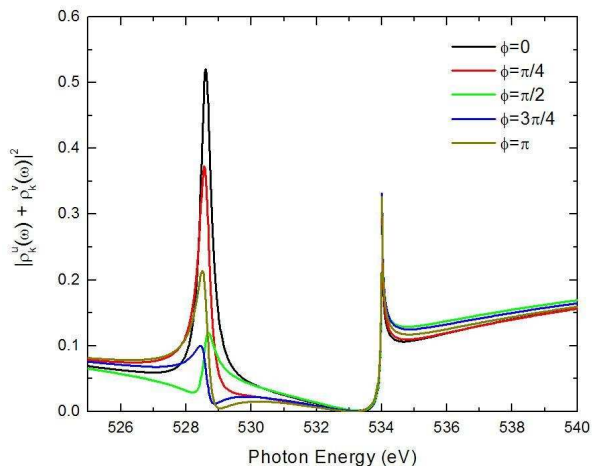


FIG. 4: Plots of the integrated intensity of resonant x-ray scattering at $q = k$, i.e. $|\rho_k^u(\omega) + \rho_k^v(\omega)|^2$ for various values of the phase between charge and strain modulations, ϕ . Notice that the spectral shape changes with ϕ . If f_D and f_R are known from absorption data, ϕ can be determined through analysis of this shape.

small. Identifying a given CDW as either Peierls-like or Wigner-like requires a quantitative comparison between the charge and lattice amplitudes. Once u_0 and v_0 have been determined by the procedure just outlined, then, a quantity of great interest is the ratio

$$W = \frac{v_0}{u_0}, \quad (19)$$

This quantity has units of length^{-1} and describes the degree to which the CDW is Wigner-like, i.e. driven by many-body interactions rather than a Peierls distortion. For example, a perfect Wigner crystal with no lattice distortion at all would have $W = \infty$. A typical Peierls CDW on the other hand, such as that in NbSe_3 , has a lattice distortion of approximately $u_0 \sim 0.01 \text{ \AA}$ and a charge amplitude of $v_0 \sim 0.1$, giving $W = 10 \text{ \AA}^{-1}$. We propose that a CDW with W less than about 20 should be considered a Peierls CDW. If $W > 100$ the CDW probably arises at least partly from many-body effects and should be considered “exotic”. It is likely that CDWs can exist over the entire continuum of values of W . It would be particularly enlightening to determine the W values for several CDW materials, such as the copper-oxides and the dichalcogenides, that also exhibit superconductivity.

V. SUMMARY

A description of resonant x-ray scattering was introduced in which the atomic scattering factor is divided into raw- and valence-dependent amplitudes, f_R and f_D . The advantage of this division is that resonant x-ray scattering from the strain wave component of a CDW tracks the average form factor $|f_R(\omega) + \langle v \rangle f_D(\omega)|^2$ whereas the charge (valence) scattering tracks only $|f_D(\omega)|^2$. In many cases f_R and f_D can be independently determined from x-ray absorption measurements on materials with different average valence, combined with Kramers-Kronig analysis. This provides a means to separately quantify the charge and strain components of a CDW. In this framework one can define a quantity “ W ” which provides a quantitative means to characterize a given CDW as Peierls-like, Wigner-like, or anywhere on the continuum between.

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refer to any charge density wave that is driven principally by many-body interactions rather than a Peierls distortion, a density wave in the dilute electron gas driven by direct Coulomb being just one example.

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